

TITLE OF INVENTION

THICK-FILM DIELECTRIC AND CONDUCTIVE COMPOSITIONS

BACKGROUND

Related Applications

5 This application is related to Application Serial Number 60/418,045,
filed in the United States Patent and Trademark Office on October 11,
2002, now United States National Application Serial Number 10/651,367,
and entitled "CO-FIRED CERAMIC CAPACITORS AND METHOD FOR
FORMING CERAMIC CAPACITORS FOR USE IN PRINTED WIRING
10 BOARDS," and Application Serial Number 60/433,105 filed in the United
States Patent and trademark Office on December 13, 2002, now United
States Application 10/633,551 filed in the United States Patent and
Trademark Office on September 16, 2003 and entitled "PRINTED WIRING
BOARDS HAVING LOW INDUCTANCE EMBEDDED CAPACITORS AND
15 METHODS OF MAKING SAME".

Technical Field

 The technical field is circuit components. More particularly, the
technical field includes powders and pastes used to form dielectric and
20 conductive elements.

Related Art

 Passive components may be embedded in printed wiring board
innerlayer panels that are stacked and connected by interconnection
25 circuitry, the stack of panels forming a printed wiring board. Embedded
capacitors are subject to requirements such as acceptable capacitance
density, low dielectric loss, high breakdown voltage, and good stability of
capacitance within specified temperature ranges. For example, Electrical
Industry Association designation Z5U requires that a capacitor's
30 capacitance vary by not more than +/-22% over the temperature range of
10-85°C, and Electrical Industry Association designation Y5V requires a
dissipation factor (Df) of less than 3%. The physical and electrical
properties of embedded components are largely dependent on the

materials used to form dielectric elements, conductive elements, and other elements of the components.

Barium titanate is commonly selected as the base material for pastes used to form high capacitance thick-film dielectrics. In components
5 such as capacitors, high dielectric constants (K) for dielectric layers are desirable because they allow for smaller capacitor size. Pure barium titanate has its maximum capacitance at its Curie point, which is at 125°C, making pure barium titanate unsuitable for many applications. The addition of dopants, however, combined with high temperature processing,
10 is a common method for shifting the Curie point of barium titanate-based materials. Specific amounts and/or chemistries of dopants may be chosen to place the Curie point where it is desired, such as at 25°C, so that the capacitance at room or near temperature is maximized.

Conventional dopants such as barium zirconate, niobium oxide,
15 and strontium titanate may not be suitable for all applications, such as firing at the lower temperatures used in thick-film processing. For example, conventional multilayer ceramic capacitors with such dopants are typically sintered for two (2) hours or more in air or in reducing atmospheres, at peak temperatures in the vicinity of 1100°C to 1400°C.
20 The conventional dopants are not effective for fired-on-foil applications performed using nitrogen-based thick-film firing profiles of shorter duration and lower temperatures.

High capacitance thick-film dielectric materials such as pastes are further constrained by the requirement of sintering aids, which must be
25 added to barium titanate in order to form a well-sintered dielectric. Conventional sintering aid glasses such as lead boro-silicates, however, have lower dielectric constants and their inclusion lowers the dielectric constant of the resulting composite. The level of glass required for conventional formation of a well-sintered dielectric often results in very low
30 dielectric constants.

Conductive pastes are used to form the capacitor electrodes of fired-on-foil capacitors. Thick-film conductive pastes typically have a metal powder component and a glass powder component dispersed in an

organic vehicle. During firing, the metal powder sinters together and the glass forms a bond with the substrate. Conventional conductive pastes that are fired on substrates of materials such as alumina are designed for conductor properties, and not for electrode properties. Therefore, the
5 pastes are generally thicker than is desirable for capacitor electrodes and contain glasses that are not chemically or physically compatible with a barium titanate-based dielectric.

SUMMARY

10 According to the first embodiment, a copper-based electrode powder comprises copper powder, cuprous oxide powder, and lead germanate glass powder. The copper-based electrode powder can be dispersed in an organic vehicle to form a screen-printing copper electrode composition, a further embodiment.

15 The conductive compositions according to the above embodiments can be used to form circuit components such as capacitors. The capacitors can be embedded in printed wiring board innerlayer panels which may in turn be incorporated into printed wiring boards. The capacitors have high dielectric constants and low dissipation factors.

20 Those skilled in the art will appreciate the above stated advantages and other advantages and benefits of various additional embodiments of the invention upon reading the following detailed description of the embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

25 The detailed description will refer to the following drawings, wherein like numerals refer to like elements, and wherein:

FIG. 1 is a table illustrating the compositions used to form dielectric paste embodiments according to the present invention;

30 **FIGS. 2A-2D** illustrate a method of forming a fired-on-foil capacitor using dielectric paste and conductive paste embodiments according to the present invention; and

FIG. 3 is table of physical and electrical properties for capacitors formed using dielectric paste and conductive paste embodiments according to the present invention.

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DETAILED DESCRIPTION

The invention concerns: (1) high dielectric constant thick-film barium titanate-based dielectric powder and paste compositions; (2) conductive powder and paste compositions; and (3) capacitors and other components formed using dielectric paste and conductive paste
10 embodiments. Thus, in this detailed description, high dielectric constant thick-film barium titanate-based dielectric powder and paste compositions are disclosed; copper thick-film electrode powder and paste compositions are also disclosed; and fired-on-foil circuit components are disclosed. The high dielectric constant thick-film barium titanate-based dielectric
15 paste compositions and the copper thick-film electrode paste compositions discussed in this specification may be used, for example, to form fired-on-foil passive circuit components. The thick-film barium titanate-based dielectric powder and paste compositions are used to form dielectrics having high dielectric constants (K) after firing.

20 The dielectrics formed from the dielectric paste compositions may be "thick-film" dielectrics having fired dielectric thicknesses in the range of about 10-60 microns. Other embodiments have thicknesses in the range of 15-50 microns. In one embodiment, dielectrics may have dielectric constants on the order of 3000, and in another embodiment, dielectric
25 constants of close to 5000. The high dielectric constant dielectrics may also have Z5U temperature stability characteristics and low dissipation factors.

The dielectrics formed from the dielectric paste compositions may have grain sizes in the range of 0.5 to 8 microns. In the embodiments
30 discussed in this specification, the term "paste" generally refers to a thick-film composition suitable for screen-printing. The thick-film pastes according to the present embodiments comprise finely divided particles of ceramic, glass, metal or other inorganic solids, having particle sizes on

the order of 1 micron or less, and an "organic vehicle" consisting of polymers dissolved in a mixture of dispersing agent and organic solvent. Specific paste compositions are discussed in detail below.

FIG. 1 is a table illustrating the individual compositions used to form thirty examples of dielectric paste according to the present invention. The ingredients are displayed in units of grams. **FIG. 1** also illustrates the ingredients comprising the dielectric powders used in forming the dielectric pastes. The ingredients that form the powders are the paste ingredients less the solvents, vehicle, oxidizer and phosphate wetting agent. **Table 1** defines the chemistry of several ingredients used in the dielectric compositions of Examples 1-30 shown in **FIG. 1**.

TABLE 1

GLASS A	lead germanate of the composition $\text{Pb}_5\text{Ge}_3\text{O}_{11}$
GLASS B	$\text{Pb}_5\text{GeSiTiO}_{11}$
GLASS C	$\text{Pb}_4\text{BaGe}_{1.5}\text{Si}_{1.5}\text{O}_{11}$
GLASS D	$\text{Pb}_5\text{Ge}_{2.5}\text{Zr}_{0.5}\text{O}_{11}$
VEHICLE	Ethyl cellulose N200 (11%) and Texanol (89%)
SOLVENT 1	TEXANOL® (available from Eastman Chemical Co.)
SOLVENT 2	DOWANOL® PPh (available from Dow Chemical Co.)
OXIDIZER	Barium nitrate powder (84%) and Vehicle (16%)

In **FIG. 1**, the powder ingredients were combined to form the high dielectric constant dielectric powder mixtures. High K thick-film dielectric pastes, according to the Examples, were formed by dispersing the high dielectric constant powder mixture into the vehicle, solvents, oxidizer and phosphate wetting agent. Dispersing was performed on a three-roll mill, and paste-like compositions suitable for screen-printing were formed. The organic vehicle provided good application properties such as good screen-printing properties. The solvents provided viscosity control, and the

phosphate wetting agent enhanced the dispersion qualities of the pastes. The oxidizer enhanced the organic component burn out for firing of the paste in nitrogen atmospheres.

5 The resulting thick-film dielectric pastes are suitable for firing under thick-film firing conditions. The dielectric pastes can be used to form components such as, for example, capacitors, and other components. A method of forming a fired-on-foil capacitor using dielectric paste embodiments of the present invention is discussed in detail below with reference to **FIGS. 2A-2D**.

10 In Examples 1-30, the thick-film glass components are inert with respect to the barium titanate and act to cohesively bond the composite together and to bond the composite to a substrate. The amounts of glass added to the compositions were selected so that the dielectric constant of the barium titanate was not excessively diluted. Lead germanate glass of
15 the composition $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ (Glass A in **Table 1**) is a ferroelectric glass that has a dielectric constant of approximately 150. Lead germanate glass can be added in quantities to form a well-sintered composite without excessively diluting the dielectric constant of the resulting barium titanate composite. Modified versions of lead germanate are also suitable. For
20 example, lead may be partially substituted by other large ionic radii valence 2 cations, such as barium. Germanium may also be partially substituted by small ionic radii valence 4 cations such as silicon, zirconium and/or titanium, as in Glasses B-D.

Pure barium titanate has its maximum capacitance at its Curie
25 point, which is at 125°C. Dopants were used to shift the Curie point to at or about room temperature (25°C) and to promote grain growth of the barium titanate. Grain growth created a higher dielectric constant with a sharper temperature coefficient of capacitance (TCC). The barium titanate of the pastes may be pre-doped or dopants may be added separately to
30 the paste. According to selected present embodiments, as shown in **FIG. 1**, small amounts of lithium salt Curie point shifters were combined with zinc fluoride to shift the Curie point and to enhance grain growth, thereby

increasing room temperature K. Lithium sources were used in Examples 4-30.

In Examples 18, 19 and 21-26, zinc fluoride was alloyed with other fluorides to achieve specific properties in conjunction with copper
5 conductive pastes A through C. Other additives were added to achieve specific properties. For example, zirconia (added in Examples 1, 8-17 and 20-26) improved resistance to etching baths routinely used in the printed wiring board industry. **FIG. 3** sets forth the resulting physical and electrical properties of the dielectric compositions when used to form capacitors.

10 **FIG. 3** is discussed in detail below.

Conductive pastes may be used to form capacitor electrodes of fired-on-foil capacitors. The electrode materials should be chosen to maximize the dielectric capacitor performance. Accordingly, the electrode should undergo physical and chemical changes during the firing process
15 that are compatible with the dielectric, such as equivalent shrinkage during sintering. In addition, chemical interactions during sintering should be selected so as to optimize electrical performance. The conductive paste should have good coverage on the dielectric to provide for high capacitance and should adhere well to the dielectric for a good dissipation
20 factor. Additional requirements include the ability to co-fire with the dielectric and to be applied as a very thin layer. **Table 2** illustrates five embodiments of copper-based pastes A, B, C, D and E according to the present invention. The ingredients are displayed in units of grams. The copper paste compositions A, through E were prepared by roll milling the
25 ingredients listed for each paste.

TABLE 2

ELECTRODE PASTE	A	B	C	D	E
Copper powder	58.4	58.0 5	57.7	61.9	64.7
Nickel powder	-	0.35	0.7	-	-
Glass A	1.7	1.7	1.7	-	1.9
Cuprous oxide powder	5.8	5.8	5.8	6.1	-
Vehicle	11.7	11.7	11.7	14.3	15.0
Texanol® solvent	12.9	12.9	12.9	17.2	17.9
Variquat® CC-9 NS surfactant (available from Barton Solvents, Inc.)	0.5	0.5	0.5	0.5	0.6

5 The copper paste embodiments sinter during firing. The desired sintering temperature is determined by the metallic substrate melting temperature, the electrode melting temperature, and the chemical and physical characteristics of any adjacent layers present during firing. For example, if dielectric and conductive pastes are used to form a capacitor, 10 the chemical and physical properties of an adjacent dielectric layer would be used to determine a desired sintering temperature for the electrode paste.

15 In the above embodiments, the sintering temperature and time at peak temperature during firing may be chosen to obtain maximum densification of the dielectric and any specific properties desired from any dopant included in the dielectric composition. High densification leads to high dielectric constants through elimination of porosity. If a capacitor is embedded inside a printed wiring board and encapsulated with epoxy resin, a density that provides for physical properties sufficient to withstand 20 the embedding process may be acceptable. The dielectric and conductive paste embodiments described above can be fired in nitrogen using a peak temperature of between about 800°C and 1050°C. Time at peak temperature may vary from 10 minutes to over 30 minutes.

Typically, the firing cycle is approximately 10 minutes at a peak of 900°C with a total time in the furnace of 1 hour.

Circuit components discussed in this specification may be formed by fired-on-foil technology. **FIGS. 2A-2D** illustrate a method of manufacturing a fired-on-foil capacitor structure **200** that was performed using the dielectric and conductive pastes discussed above. **FIG. 2A** is a front elevational view of a first stage of manufacturing the capacitor structure **200**. In **FIG. 2A**, a copper foil **210** was pretreated by applying and firing an underprint **212** to form the first electrode. The underprint **212** was formed by screen-printing a conductive paste layer through a 400 mesh screen to form a square area of 1.75 cm by 1.75 cm. The paste was dried at 120°C for 10 minutes in air in an oven, and the foil was fired at 900°C in nitrogen for 10 minutes at peak temperature.

A dielectric paste was screen-printed onto the underprint area of the pretreated foil **210** so that the dielectric area was contained within the underprint area. The dielectric paste was screen-printed through a 230 mesh screen to form a dielectric layer **220** that was 1.25 cm by 1.25 cm. in area. The first dielectric layer **220** was then dried at 120°C for 10 minutes in air in an oven. Referring to **FIG. 2B**, a second dielectric layer **225** was applied and dried. The total thickness of the two dried dielectric layers was approximately 30 microns.

Referring to **FIG. 2C**, a second or top electrode **230** was formed by screen-printing a conductive paste over the second dielectric layer **225**. The second electrode **230** was 0.9 cm by 0.9 cm in size. In some cases, the second electrode was formed using the same paste as was used to form the underprint **212**. In other cases, the second electrode was of a different composition than that of the underprint **212**. The resulting article was then dried at 120°C for 10 minutes in air and then fired at 900°C in nitrogen for 10 minutes at peak. The finished capacitor **200** is shown in **FIG. 2D**. During firing, the glass component of the dielectric paste softens and flows, coalesces, and encapsulates the barium titanate to form a fired dielectric **228**. The dielectric **228** had a fired thickness of between 20 and

24 microns and the second electrode **230** had a fired thickness of between 3 and 5 microns.

Examples 1-30 of the dielectric paste compositions illustrated in **FIG. 1** and the electrode paste compositions A-E illustrated in **Table 2** were evaluated by forming capacitors using the methodology illustrated in **FIGS. 2A-2D**. The capacitors were then tested using a Hewlett Packard 4262A LCR meter for capacitance and dissipation factor (Df) at 1 KHz and 10 KHz. The thickness of the dielectric was measured and the dielectric constant was calculated from the following formula:

$$K = \frac{C * T}{0.885 * A}$$

where C = capacitance in nanofarads (nF)
T = thickness in microns
A = area in square cm
0.885 = a constant.

FIG. 3 is table of physical and electrical properties for the capacitors formed from the dielectric paste and conductive paste embodiments and tested at 10KHz. The capacitances were tested at several temperatures between -55°C and 125°C using a Hewlett Packard 4278A LCR meter to establish the position of the Curie point. The data in **FIG. 3** show that high dielectric constants were obtained by use of barium titanate and specific combinations of dopants in combination with specific electrode and underprint compositions. The combinations placed the Curie points close to room temperature and grew large barium titanate grains. A better dissipation factor Df was observed when the Curie point was less than room temperature.

The Curie point of the dielectric paste embodiments were shifted to room temperature by a lithium source. Examples 1-3 illustrate that without a lithium source (lithium fluoride or lithium carbonate), the Curie point remains at 125°C. As shown in examples 4 and 5, a lithium source shifted the Curie point. As shown in example 6, the addition of calcium fluoride

reduced this effectiveness and shifted the Curie point only to 105°C. This effect was presumably due to the high melting point of calcium fluoride. Example 7 shows that addition of barium fluoride and manganese fluoride in quantities to form a low melting point combination helped the lithium source shift the Curie point very effectively. Thus, the lithium source was most effective in shifting the Curie point when it was in a quite fluid form at the firing temperature. Lithium on its own or in combination with the fluorides in examples 6 and 7, however, did not facilitate growth of the barium titanate grains.

As shown in dielectric examples 8 through 26, growth of the barium titanate grains was most effectively facilitated by a zinc source. Growth of the barium titanate grains produced high dielectric constants by sharpening the Curie point. Zinc sources are corrosive to barium titanate, dissolving small particles and precipitating them onto larger particles, thus growing the average particle size of the barium titanate. The zinc source in the above examples was zinc fluoride. In examples 10 through 17, zinc fluoride was used alone with the lithium source, and high dielectric constants were realized. However, because zinc fluoride melts at 947°C, it may not be optimally effective in growing the grains when the composition is fired at 900°C. As shown in examples 18 through 29, however, when fluxed with other fluorides to produce a low melting point composition, the zinc fluoride was very effective in growing the barium titanate grains at 900°C. As a result, very high dielectric constants were realized. Effective fluoride combinations to produce low melting point combinations included barium fluoride and zinc fluoride combined with the lithium source.

Examples 9, 13, 16 and 19 show the effects of nickel doping of the capacitor electrode. The nickel addition to the copper pastes had a beneficial effect in that it moved the Curie point to lower temperatures.

Examples 27 and 28 show the effects of omitting glass A from the underprint composition and from both the underprint and top electrode compositions. The capacitance and Df were satisfactory, and the Curie point was shifted slightly to lower temperatures. Example 29 shows the

effect of omitting copper oxide from the preprint. The electrical data were acceptable. However, in example 30, when copper oxide was omitted from both the preprint and the top electrode, the dielectric constant was reduced significantly and the Df was increased significantly.

5 Compositions such as example 18 may be tailored using fluoride and lithium source combinations. These compositions have very low melting points in combination with specific electrode compositions and very high room temperature dielectric constants, such as 4800. Such compositions, however, have sharp Curie peaks. If a flatter response of
10 the dielectric constant to temperature is required, use of less fluid dopant combinations and/or additions of zirconia may be employed. Such compositions achieve dielectric constants close to 3000. Zirconia also has an additional benefit in that it renders the dielectric more resistant to the acid etchants used in printed wiring board manufacture. Other additives,
15 such as titania, may also be added to control grain growth and improve etch resistance. Compositions may also be tailored to have lower K but with very low dissipation factors at room temperature by positioning the Curie point at low temperatures.

 Capacitors and other components and elements produced using
20 the paste and powder embodiments of the present invention are suitable for embedding in printed wiring boards. For example, the capacitor 200 illustrated in **FIG. 2D** may be laminated to a laminate material and etched to create an innerlayer panel with embedded capacitors. The innerlayer panel may be laminated to additional innerlayer panels to form a printed
25 wiring board.

 The foregoing description of the invention illustrates and describes the present invention. Additionally, the disclosure shows and describes only selected preferred embodiments of the invention, but it is to be understood that the invention is capable of use in various other
30 combinations, modifications, and environments and is capable of changes or modifications within the scope of the inventive concept as expressed herein, commensurate with the above teachings, and/or within the skill or knowledge of the relevant art.

The embodiments described hereinabove are further intended to explain best modes known of practicing the invention and to enable others skilled in the art to utilize the invention in such, or other, embodiments and with the various modifications required by the particular applications or
5 uses of the invention. Accordingly, the description is not intended to limit the invention to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments, not explicitly defined in the detailed description.